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INVESTIGATION OF HYDRAZINE-AIR
FUEL CELL SYSTEMS

Progress Report No. 4

by

Seigo Matsuda, John C. Smith,
and Bernard P. Sullivan

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INVESTIGATION OF HYDRAZINE-AIR
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Progress Report No. 4
15 November 1966 to 15 February 1967

Contract No. DA28-043-AMC-01996(E)
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Prepared by

S. Matsuda, J. O. Smith

and B. P. Sullivan

Monsanto Research Corporation
Boston Laboratory
Everett, Massachusetts 02149

for

U. S. Army Electronics Command
Fort Monmouth, New Jersey

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SUMMARY

In the fourth quarter, new materials for anode and separator were investigated, and experiments were carried out to optimize the treatment of anode with catalyst poisons ($S^=$), and the catalyst loading for NH_3 oxidation. Full cell testing (3 x 3 in.) again revealed the significant improvement in performance of both the hydrazine anode and also of the combined cathode imparted by $S^=$ poisoning. Very active non-noble-metal catalysts such as Ni-B, Co-B and Ni-P can be used if the electrode is properly poisoned. Generally, these catalysts give very active potentials but low fuel efficiencies by excess decomposition of hydrazine fuel.

Publications, Lectures, Reports, & Conferences

None

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I. INTRODUCTION

A. BACKGROUND

This is the fourth quarterly report on the investigation of hydrazine (N_2H_4)-air fuel cell systems under contract DA28-043-AMC-01996(E) with the U.S. Army Electronics Command, Power Sources Division, Electronic Components Laboratory, Fort Monmouth, New Jersey.

The work is aimed at acquiring a basic understanding of the components of the cell. An additional objective is to find ways to improve presently operating systems by utilizing the knowledge obtained during the contract.

In the first quarter, some important determinations were made, particularly concerning the mechanism of the hydrazine anode reaction. The mixed potential concept seemed to explain best the various effects observed on the hydrazine anode. During the second quarter, a more detailed investigation was made of parameters affecting anode performance, including effects of composition, temperature, and impurities in the electrolyte. In addition, some analysis was devoted to possible approaches to improving anode performance, based on the mechanism of the anode reaction. Results indicated that the electrode performance can be significantly improved by some of the approaches undertaken. In the third quarter, in addition to further fundamental investigation of the other components of the fuel cell system, these improved anodes were tested in a scaled-up 3 x 3 inch full cell system.

Since the second quarter, study of NH_3 scrubbing has also been continued, and the feasibility of catalytic oxidation of NH_3 to nonhazardous water and nitrogen gas was demonstrated.

B. FOURTH QUARTER OBJECTIVES

Objectives for this quarter were:

(1) to continue study of the electrode substrate, particularly of commercially available porous membrane of various metals.

(2) to optimize catalyst poisoning treatment.

(3) to study non-noble metal catalysts.

(4) to continue study of the NH_3 decomposition reactor.

(5) to study separator materials.

(6) to continue 3 x 3 inch full cell testing on promising materials.

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II. PHASE I. STUDY OF HYDRAZINE ANODE

A. BACKGROUND

In the first quarterly report, the mixed potential concept was suggested as the most probable mechanism for the hydrazine electrode, which seemed to consist of multiple reduction-oxidation systems existing simultaneously on the electrode surface. In the second quarterly report, possible approaches for improving the performance characteristics of the hydrazine anode were discussed, utilizing this concept. Experimental results also showed that some of the approaches, particularly proper selection of the substrate and use of catalyst poisons, improved the performance characteristics of the anode. During the third quarter, a large number of porous nickel plaque electrodes treated in various ways were tested, and some of these electrodes seemed very promising in giving high fuel efficiencies, low NH_3 evolution, and reasonably active potentials.

During this quarter, several tasks were continued to improve the overall performance of the present N_2H_4-air full cell systems, particularly regarding problems associated with the hydrazine anode.

B. TASK I. STUDY OF ELECTRODE SUBSTRATE

Commercially available porous membranes of various metals were purchased from Union Carbide Co. These membranes were prepared by powder sintering and hot rolling and have uniform thicknesses (about 0.01 inch) and uniform micropore distributions.

All electrodes for testing were prepared as 2 x 2 inch squares. A piece of pure nickel wire was spot-welded as an electrical lead at the edge of one side of the square. In view of practical applications, measurements of the present tests were limited to the potentials at open circuit (OCP) and at 100 mA/cm^2, the rate of gas evolution, and the NH_3 content in the evolved gas. Consequently, the apparatus used for the tests was the one discussed in detail in the first quarterly report (Figure 1). Electrolyte used for the tests was 5M KOH containing 2M N_2H_4. The testing temperature was $70° \pm 1°C$.

Results, which are summarized in Table 1, indicate that Ni substrate gave the highest potential as well as the highest gassing, and the highest NH_3 content in the evolved gas. All other substrates gave almost no excess gassing and very low NH_3 content, but much lower potentials than Ni.

Power Supply

Nu Jol

Water

Constant Temperature Water Bath

Luggin
Capillary

Testing
Electrode

Pt
Plated Pt
Counter Electrode

He Purge

3-Way Stopcock

To Calomel
Electrode

Electrolyte

dil. HCl

Sintered Glass

conc. H₂SO₄

Rubber
Tubing

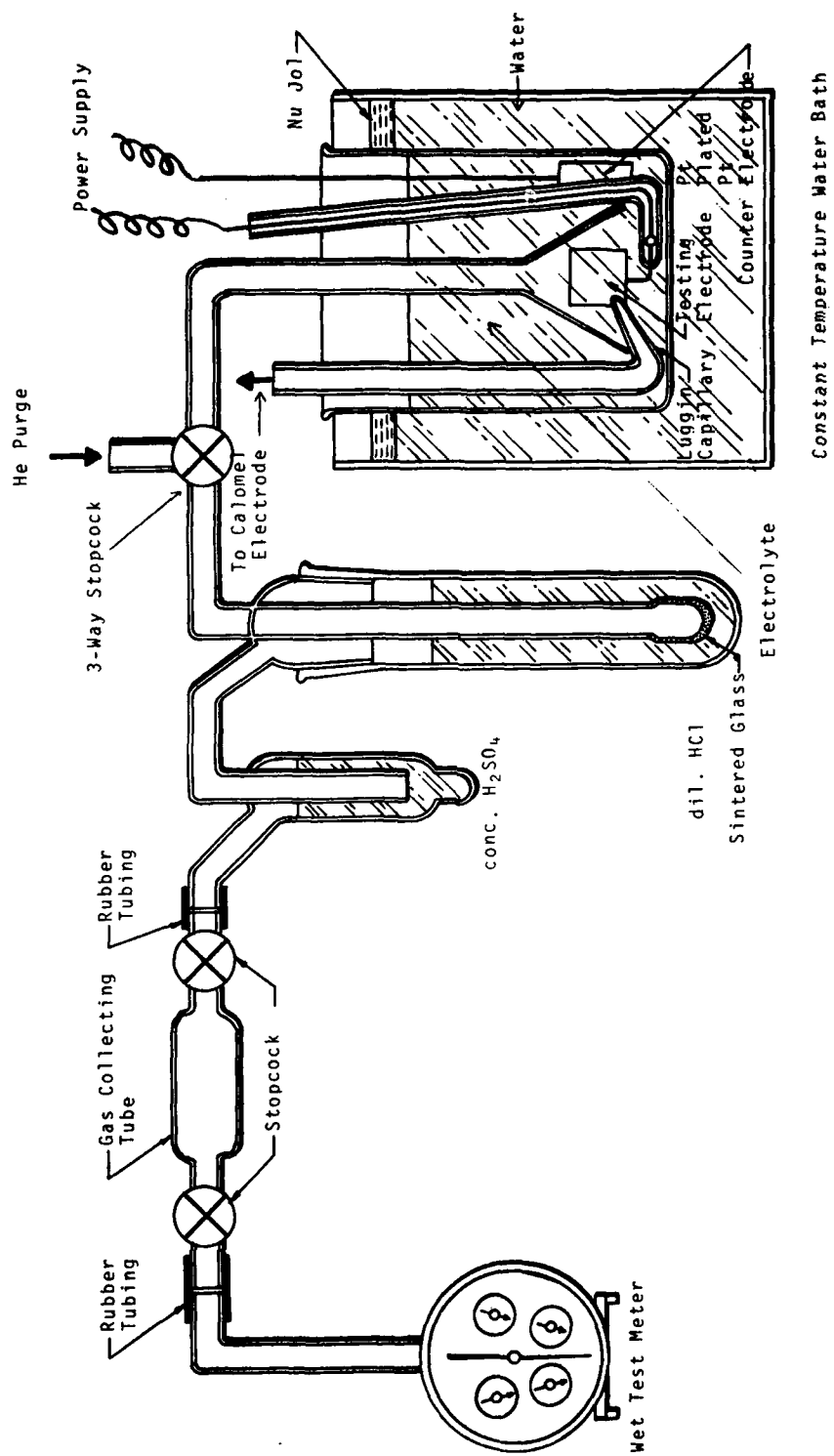Gas Collecting
Tube

Stopcock

Rubber
Tubing

Wet Test Meter

Figure 1. Reaction Generator and Gas Collecting Train

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TABLE 1

PERFORMANCE OF VARIOUS POROUS METAL MEMBRANES AS HYDRAZINE ANODES

| Electrode* No. | Substrate Metal and Treatment | Electrode Potential Volts vs SCE | | Excess Gassing cc/min at 100mA/cm² | | NH₃ Content in the Evolved Gas, % at 100mA/cm² | |
		OCP	at 100mA/cm²	OCP	at 100mA/cm²	OCP	at 100mA/cm²
1.	Fe, No catalyst	-1.17	-1.07	~0	~0	~0	0.10
2.	Fe + 10mg/in² Pd	-1.17	-1.08	~0	~0	~0	0.03
3.	Ni:NR-40,No catalyst	-1.33	-1.22	~0	~0	~0	0.18
4.	Ni:NR-40+10 mg/in² Pd	-1.25	-1.20	13	190	0.17	0.99
5.	Ni:NU-40,No catalyst	-1.19	-1.09	~0	~0	~0	0.06
6.	Ni:NU-40+10 mg/in² Pd	-1.22	-1.18	23	175	0.20	0.41
7.	Cu:CU-40, No catalyst	-1.25	-0.94	~0	~0	~0	0.05
8.	Cu:CU-40+10 mg/in² Pd	-1.23	-1.05	~0	~0	~0	0.05
9.	Ag, No catalyst	-1.25	-1.10	~0	~0	~0	0.04
10.	Ag+10 mg/in² Pd	-1.20	-1.09	~0	~0	~0	0.33

*Electrode No. 1 & 2: Porous Fe sheet, thickness 0.006", pore distribution 1.2 ~ 3.3μ, voids 27%.
Electrode No. 3 & 4: Porous Ni sheet, thickness 0.008", mean pore diameter 4.0μ, voids 40%.
Electrode No. 5 & 6: Porous Ni sheet, thickness 0.012", mean pore diameter 11.6μ, voids 40%.
Electrode No. 7 & 8: Porous Cu sheet, thickness 0.007", mean pore diameter 6.5μ, voids 40%.
Electrode No. 9 & 10: Porous Ag sheet, thickness 0.0085", pore distribution 12 ~ 21μ, voids 37%.

C. TASK II. STUDY OF CATALYST POISONS

Experimental results in the previous quarters showed that the performance characteristics of the hydrazine anode were significantly improved by treating the electrodes with the proper amount of catalyst poisons, particularly $S^=$ and $Se^=$ ions or by adding the proper amount of these catalyst poisons to the electrolyte.

Since it is believed that the catalyst poisons added to the electrolyte were eventually absorbed onto the electrode and that in the meantime there might be a possible undesirable effect on the cathode performance, pretreatment of the electrode with the catalyst poisons were considered better than adding them into the electrolyte. During this quarter, then, experiments were carried out to optimize the amount of the catalyst poisons, $S^=$, for the pretreatment of the electrode.

Sections of MRC anode (1 x 1 in.) were placed in the various amounts of $10^{-4}M$ Na_2S solution for 24 hours and then were thoroughly washed in distilled water. Using the apparatus shown in Figure 1, the open circuit potential and the open circuit gas rate on these electrodes were determined in the electrolyte, 5M KOH + 2M N_2H_4, at 70°C.

Results are summarized in Figure 2 which shows the saturation of the effect at around 50 to 70 cc of solution per $inch^2$ of electrode. Qualitative chemical analysis for $S^=$ in the remaining solution showed that there was no $S^=$ in 25 cc/$inch^2$, a trace in 50 cc/$inch^2$, and more in the larger amount of solution.

NH_3 content in the evolved gas from the electrode treated with 75 cc of solution per $inch^2$ of electrode was only 0.03%.

D. TASK III. STUDY OF NON-NOBLE METAL CATALYSTS

1. Background

One of the very critical problems associated with overall development of fuel cells is development of high efficiency (or highly active) and low cost (non-noble metal) catalysts. Difficulties with this task include the high complexity of the electrocatalysis process; none of the existing mechanisms and theories on heterogeneous catalysis directly apply. There are also difficulties in preparing proper catalytic non-noble metal compounds.

It is, of course, true that the hydrazine-air fuel cell has a significant engineering advantage over many other fuel cell systems owing to the high reactivity of its water-soluble hydrazine fuel. This high reactivity of hydrazine results in a very small loss of potential due to activation polarization even at very high current
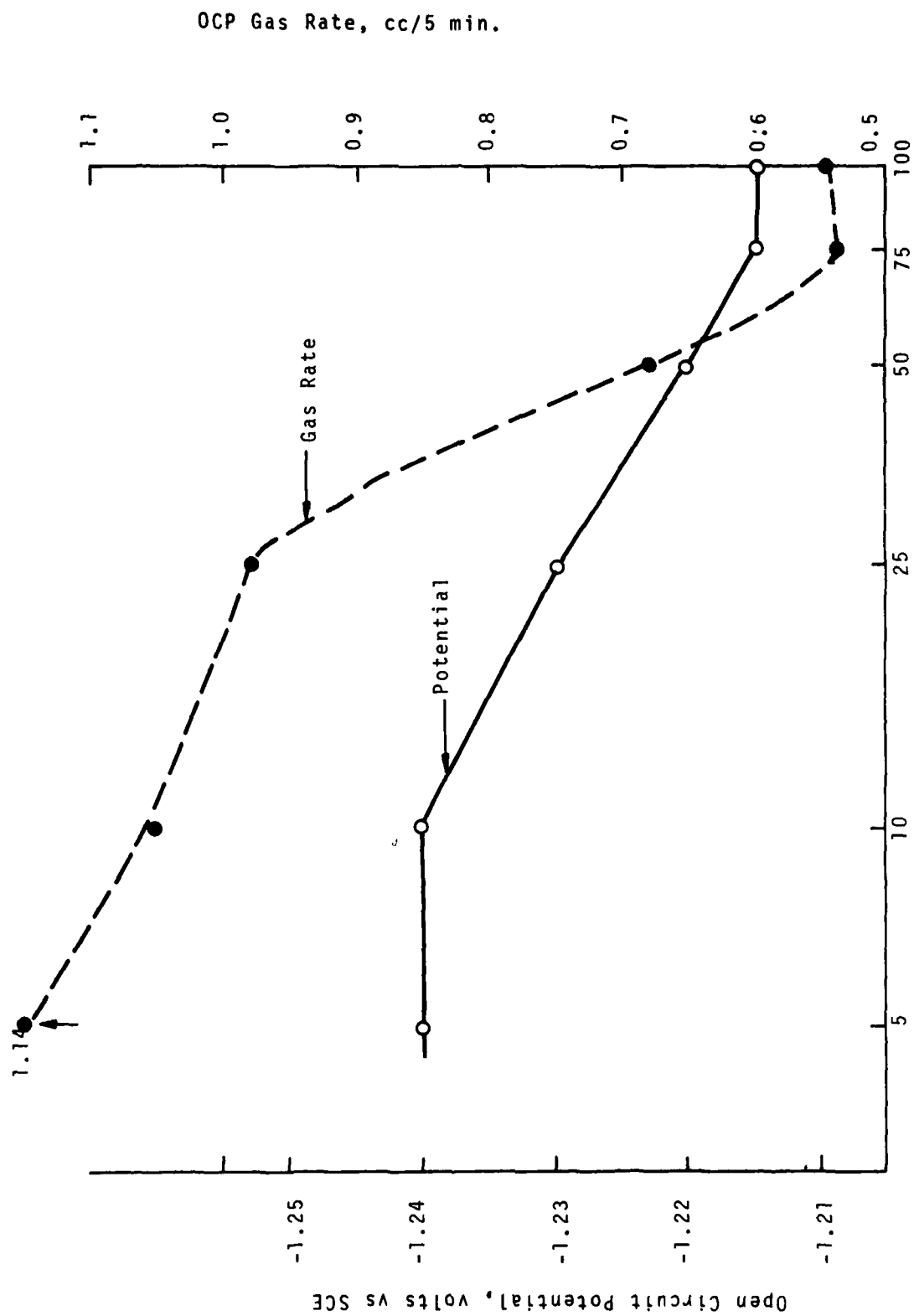
5

OCP Gas Rate, cc/5 min.

Gas Rate

Potential

1.14

Amount of 10⁻⁴ M Na₂S Solution, cc/inch² electrode

Figure 2. Optimization of Catalyst Poisoning

Open Circuit Potential, volts vs SCE

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densities. The high solubility and stability of hydrazine in caustic solutions also enables us to employ a caustic electrolyte containing a high concentration of hydrazine fuel, thus minimizing concentration polarization at high current densities.

Previous experimental results revealed that because of the high concentration and reactivity of hydrazine fuel, even a porous nickel plaque without any catalyst present has reasonable activity, although its active life is limited. Considering the high cost and limited national supply of the precious metals that are presently used in the operating systems, investigation of non-noble-metal catalysts will be important to the future development of the fuel cell.

2. Interstitial Compounds of Transition Metals

Interstitial compounds of transition metals, borides, carbides, nitrides, carbonitrides, and nitrocarbides, have generally good metallic conductivities, and many of them are very stable in caustic. The availability of various catalytically promising compounds, synthesized by the U.S. Bureau of Mines for NASA, offered us an opportunity to investigate their electro-catalytic activities for the oxidation of hydrazine.

During this quarter, the compounds listed in Table 2 were supplied by the Bureau of Mines. Methods of preparation of these compounds are given in the literature (ref. 1).* Since we were informed that these catalysts are pyrophoric and that they were shipped out in small glass bottles encapsulated under an inert gas atmosphere, they were preconditioned before they were fully exposed to the air. All capsules were placed in a dry box and then carefully opened under chemically pure argon. A small amount of air (corresponding to less than 1%) was then mixed into argon stream. After a sufficient time for stabilization air was very gradually increased to the atmospheric level. This process took several hours to complete.

Since some of the compounds were too coarse for use in our electrode manufacturing methods, they were ground and sieved to -400 mesh particles. Although it is desirable to grind in an inert atmosphere, the grinding was actually carried out in air and resulted in loss of one compound (sample No. 18N) by ignition.

No electrodes containing these compounds were tested during this quarter.

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*1. Bureau of Mines, "Development of an Improved Oxygen Electrode for Use in Alkaline H_2-O_2 Fuel Cells," under contract NASA W-12,300, Report for period July 1 - September 30, 1966.

TABLE 2

INTERSTITIAL COMPOUNDS APPLIED BY
THE BUREAU OF MINES DURING THIS QUARTER

Prepared from an Alkali Promoted Magnetite*

	Sample No.	X-ray Analysis
Carbides		
	10C	Θ-Fe_3C, α-Fe
	11C	χ-Fe_2C
	14C	Θ-Fe_3C
Nitrides	1N	ϵ-Fe_3N, γ'-Fe_4N
	2N	γ'-Fe_4N, ϵ-Fe_3N
	5N	ϵ-Fe_3N, γ'-Fe_4N
	6N	ϵ-Fe_3N, ζ-Fe_2N
	9N	ζ-Fe_2N
	10N	ϵ-Fe_3N
	19N	ζ-Fe_4N, ϵ-Fe_3N
	21N	γ'-Fe_4N, ϵFe_3N
Nitrocarbides		
	2NC	χ-$Fe_2X(C,N)$, ϵ-$Fe_2X(C,N)$
	3NC	ϵ-$Fe_2X(C,N)$
	5NC	Θ-$Fe_3X(C,N)$
Carbonitrides		
	1CN	ϵ-$Fe_2X(C,N)$
	2CN	ϵ-$Fe_2X(C,N)$
	5CN	ϵ-$Fe_2X(C,N)$
	9CN	ϵ-$Fe_4X(C,N)$

Prepared from leached Raney iron**

Carbides	2C	ϵ-Fe_2C, Fe_3O_4
	4C	χ-Fe_2C, Fe_3O_4
	7C	χ-Fe_2C
	12C	ϵ-Fe_2C, α-Fe
	15C	Θ-Fe_3C
	23C	ϵ-Fe_2C, α-Fe(trace)
Nitrides	13N	ϵ-Fe_3N
	17N	ϵ-Fe_3N
	18N	ζ-Fe_2N, ϵ-Fe_3N
	20N	ϵ-Fe_3N

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TABLE 2 (cont'd)

	Sample No.	X-ray Analysis
<u>Nitrocarbides</u>	1NC	ε-$Fe_2X(C,N)$, Fe_3O_4
	4NC	ε-$Fe_2X(C,N)$
	7NC	Θ-Fe_3X
<u>Carbonitrides</u>	3CN	ε-$Fe_2X(C,N)$
	4CN	ε-$Fe_2X(C,N)$

<u>Prepared from coprecipitated oxides of Fe and Ag</u>

<u>Carbonitrides</u>

Ratio	Sample No.	Xray Analysis
3Fe/1Ag	6CN	ε-$Fe_2X(C,N)$,Ag
1Fe/1Ag	7CN	ε-$Fe_2X(C,N)$,Ag
1Fe/3Ag	8CN	Ag, ε-$Fe_2X(C,N)$

* Fe_3O_4:93.46%   MgO:4.61%, K_2O: 0.57%
    SiO_2:0.71% $C_{r2}O_3$:0.65%

**   Fe: 90.0%
      Al: 1.4
      Na: 0.03

3. Non-Noble-Metal Catalysts on Ni Plaque

In starting our investigation of non-noble-metal catalysts, some known catalysts were tested first. Squares (2 x 2 in.) of porous nickel plaque were first soaked with 10% $NiCl_2$ solution (one with $CoCl_2$), dried, then reacted with 10% of various reducing agent solutions, and finally washed in distilled water.

Using the apparatus shown in Figure 1, the performance characteristics of these electrodes were determined in 5M KOH + 2M N_2H_4 at 70°C.

Results are shown in Table 3. All catalysts, except one reduced with $Na_2S_2O_3$, are very active, but all gas at very high rates.

After the regular tests, $10^{-3}M$ Na_2S solution was added dropwise to the testing electrolyte. As the amount of sulfide increased in the electrolyte, gassing gradually decreased. When no gassing was observed, the electrode potentials were between -1.20 and -1.25 volt at open circuit and -1.17 to -1.20 volts at 100 mA/cm^2. This suggested that these catalysts can replace noble metal catalysts if they are properly poisoned.

E. TASK IV. STUDY OF DECOMPOSITION OF NH_3

Results in the previous quarters suggested that NH_3 formation along with the electrochemical oxidation of N_2H_4 is more or less essential although selection of a proper substrate and catalysts or treatment of the electrode with catalyst poisons can reduce the amount of NH_3 to some extent. Consequently, efforts were devoted to eliminating NH_3 from the exhaust gas by its catalytic oxidation to harmless water and nitrogen gas. Among a number of catalysts tested, platinum black chemically plated on porous Ni plaque was the best, and was practically the only catalyst that satisfactorily oxidized NH_3 at a relatively low temperature ($\sim$150°C).

During this quarter, experiments were carried out to determine the minimum amount of the catalyst necessary for a given condition.

Porous Ni plaque chemiplated with Pt black from chloroplatinic acid solution was cut into small pieces, approximately 1/4 x 1/4 inch or smaller. A known amount of these pieces was packed in the reaction zone of the reactor tube shown in Figure 3. One liter/min of N_2, which was added with 5% NH_3, and two times of stoichiometric air saturated with water for the complete oxidation of NH_3 was passed through the reactor heated to 150°C.

Analysis of the exit gas indicated that at least 0.8 gram of Pt is needed to oxidize 100% of NH_3 added to the stream.

These data will be utilized to design a prototype reactor that can be attached to the operating fuel cell stack units.

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TABLE 3

HYDRAZINE ANODE PERFORMANCE OF Ni PLAQUE ELECTRODE CATALYZED WITH VARIOUS NON-NOBLE-METAL CATALYSTS

Electrode No.	Reducing Agent	Electrode Potential Volts vs SCE		Excess Gassing		NH_3 Content, %	
		OCP	at 100mA/cm²	OCP,cc/min	at 100mA/cm²	OCP	at 100mA/cm²
1.	Blank (Ni Anode)	-1.31	-1.26	45*	80*	1.1	0.82
2.	$NaBH_4$	-1.32	-1.27	55	40	0.90	0.62
3.	$CoCl_2 + NaBH_4$	-1.30	-1.28	110**	600**	7.20	8.30
4.	H_2NaPO_2	-1.30	-1.25	7.5	60	-	0.83
5.	$Na_2S_2O_3$	-1.18	-1.03	0	0	0	0.005

* Only for the first few hours; then they quickly go down to about one half of these values.

** For the first five hours; then gradually went down to much lower values.
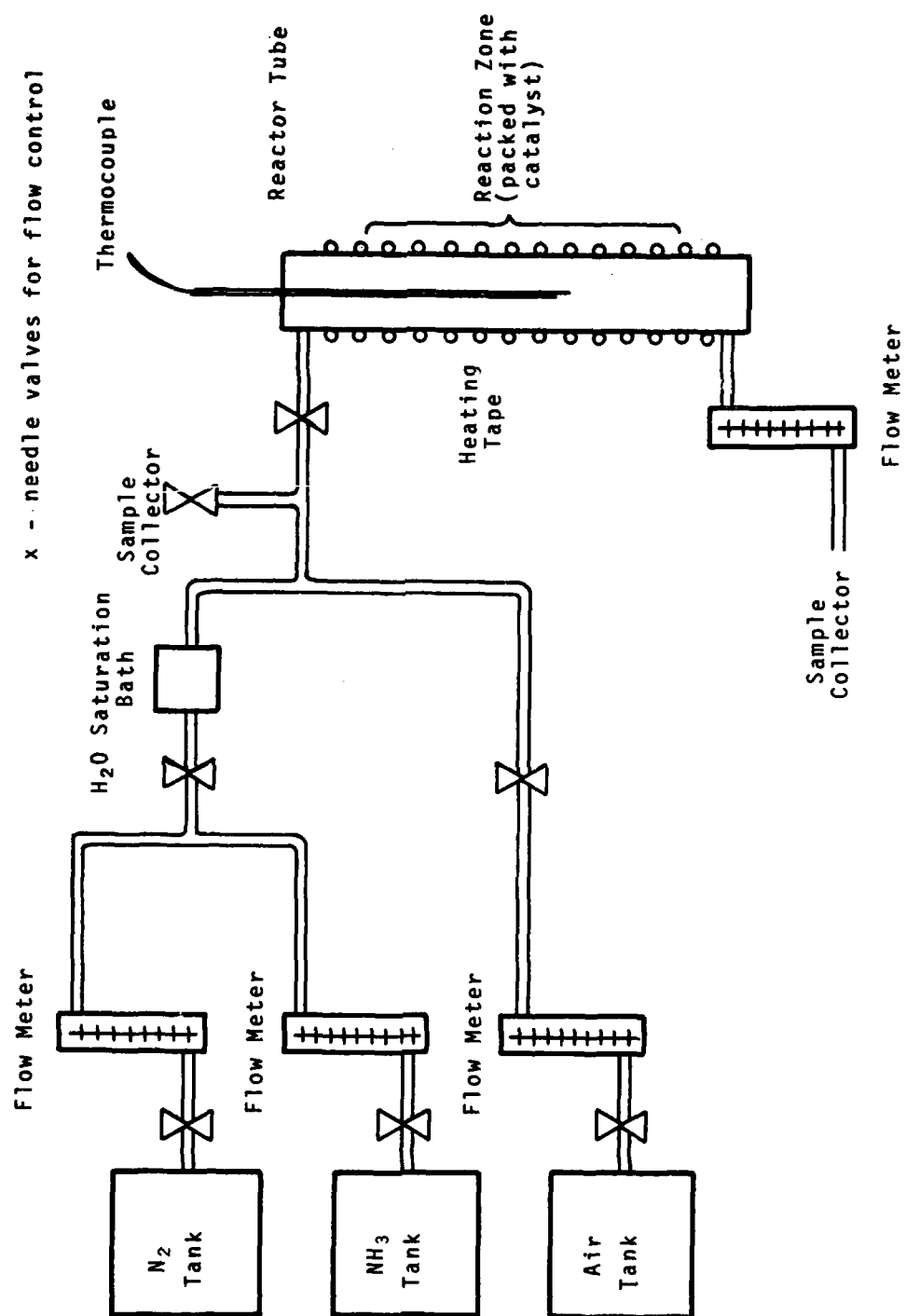
Figure 3. Schematic Diagram of an Apparatus for NH_3 Decomposition Test

x - needle valves for flow control

Thermocouple

Reactor Tube

Reaction Zone
(packed with
catalyst)

Heating
Tape

Flow Meter

Sample
Collector

Sample
Collector

H_2O Saturation
Bath

Flow Meter

Flow Meter

Flow Meter

N_2
Tank

NH_3
Tank

Air
Tank

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III. PHASE II. INVESTIGATION OF SEPARATOR MATERIAL

A. CORROSION TEST

Separator materials, which were previously tested for N_2H_4 permeation and IR drop, were exposed to the electrolyte for three months to determine their chemical and physical stability in the environment of operating fuel cells.

The testing solution was 5M KOH + 2M N_2H_4 at 70°C. Results are summarized in Table 4 and are not favorable. Except for some asbestos samples, the only material that did not show any change was polypropylene which was rather poor in stopping N_2H_4 permeation in previous electrochemical testing. However, it may be still possible to use some materials that simply discolored if their essential properties as a separator did not change drastically.

B. SEPARATORS WITH OXIDE

Fine powders (-300 mesh) of various stable oxides were uniformly dispersed into polyvinylalcohol solution, poured onto a flat glass surface, and dried in air to form a thin membrane. These membranes were tested with the MRC air cathode for N_2H_4 permeation and IR drop.

The apparatus and the experimental method for testing separators were the same as those used in the previous quarters. Figure 4 shows the half cell testing unit. Separators tested were placed on the front surface of the electrolyte side of MRC air cathode.

The electrolyte was 5M KOH solution containing 2M N_2H_4. The air cathode polarization data were taken at 50 and 75°C by using an interrupting bridge (Kordesch-Marko Bridge) and IR-free potential and IR drop were used to qualify the separator characteristics of testing materials.

Results are summarized in Table 5. Membranes containing the higher ratio of oxide to PVA than those listed in Table 5 did not have a sufficient mechanical strength.

Results indicated that many of these membranes gave better IR-free potentials than the control (fuel cell grade asbestos), but IR drops at 100 mA/cm^2 were generally higher than that of the control.

Since the thicknesses of these membranes were not well controlled, the fabrication process must be improved before quantitative analysis is made.

Table 4

CORROSION TEST OF SEPARATOR MATERIALS

Testing solution: 5M KOH + 2M N_2H_4 at 70°C
Testing period: 3 months

Material	Results
Viskon cotton-cellulose[†]	Discolored, 20% shrinkage
Viskon rayon-cellulose[†]	1.5% shrinkage
100% polypropylene FT-2140	No physical change, 12% wt. loss
Pellon	Discolored, badly disintegrated
Webil EM-312	Discolored (yellow), no physical change
Webil EM-470	Disintegrated
Dynel	Disintegrated
MRC membrane* #1	Discolored, washed-out
MRC membrane** #2	Discolored, washed-out
MRC membrane*** #3[†]	Discolored
Permion paper[†]	Discolored, 20% shrinkage
Nylon	Disintegrated
Acrilan	Disintegrated
ACCO #2 asbestos	Discolored, disintegrated.
ACCO #1 asbestos	No change (swelled)
Fuel Cell Grade Asbestos	No change (swelled)

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*   Vinylpyridine 78% - Methacrylic acid 22%
**   Vinylpyridine 57% - Methacrylic acid 43%
***   PVA Film
†   Some weight gain
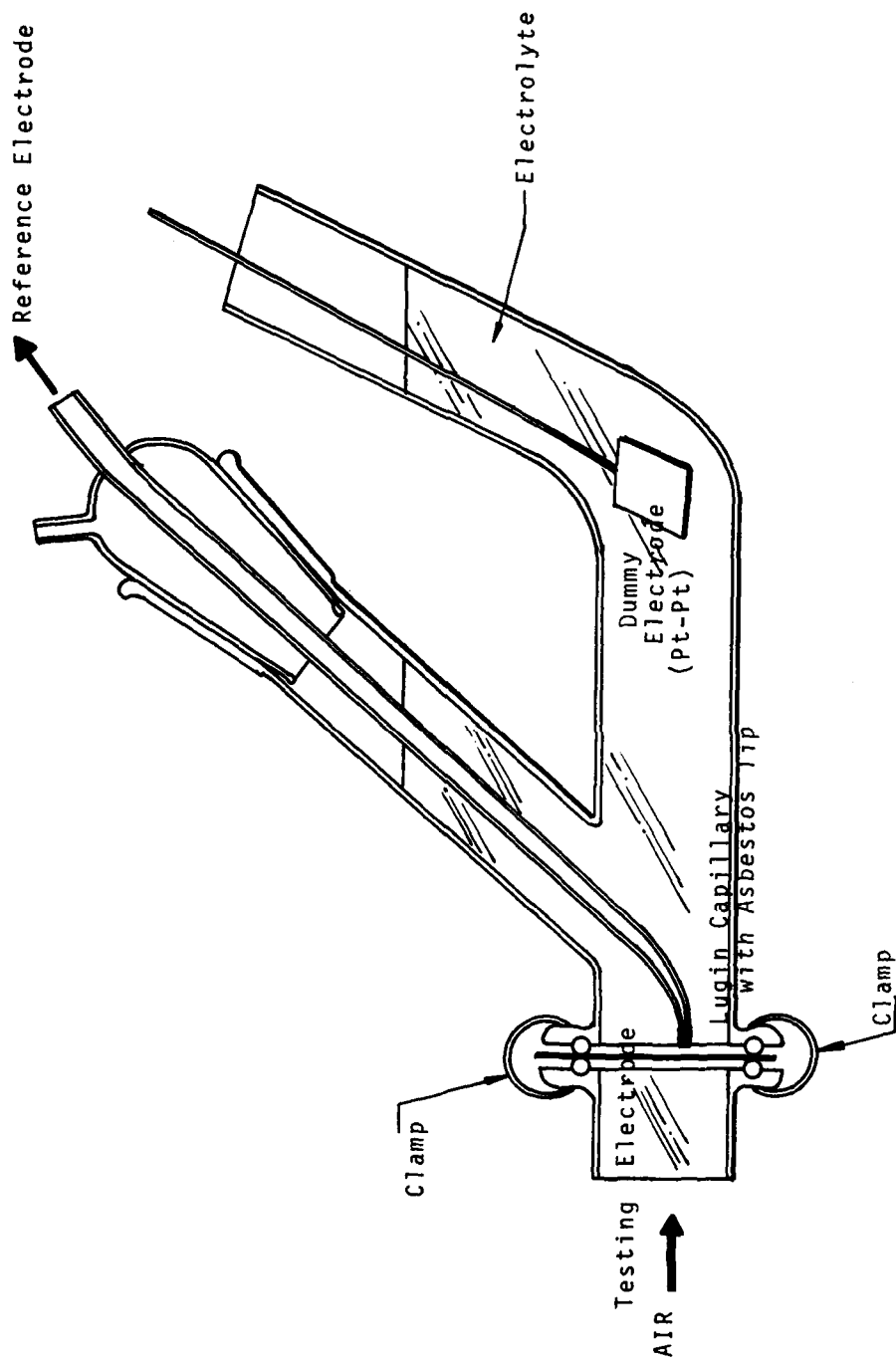
Figure 4. Half Cell for Polarization Study

Reference Electrode

Electrolyte

Dummy
Electrode
(Pt-Pt)

Lugin Capillary
with Asbestos 17p

Testing Electrode

Clamp

Clamp

Testing
AIR

15

TABLE 5

SEPARATOR TESTS

ELECTROLYTE: 5M KOH+2M N_2H_4

| Separator | | | IR Free Potential, volt vs SCE at Various C.D., ma/cm² | | | IR Drop |
Oxide	PVA	Temp.°C	OCP	at 50mA/cm²	at 100mA/cm²	at 100mA/cm²
MgO,0.1gr.	5%,40gr.	50	-0.17	-0.28	-0.32	0.21
"		70	-0.22	-0.25	-0.28	0.12
MgO, 1gr.	5%,40gr.	50	-0.23	-0.28	-0.33	0.38
"		70	-0.22	-0.24	-0.28	0.22
MgO, 1gr.	5%,20gr.	50	-0.20	-0.24	-0.25	0.27
		70	-0.19	-0.23	-0.25	0.28
MgO, 1gr.	5%,10gr.	50	-0.22	-0.25	-0.28	0.44
		70	-0.21	-0.24	-0.27	0.42
MgO, 1gr.	5%,4gr.	50	-0.24	-0.26	-0.27	0.12
		70	-0.21	-0.25	-0.27	0.28
MgO, 5gr.	5%, 10gr.	50	-0.25	-0.26	-0.27	0.22
		70	-0.20	-0.24	-0.25	0.21
MgO,0.1gr.	5%,40gr.*	50	-0.25	-0.27	-0.30	0.09
		70	-0.22	-0.27	-0.34	0.31
$SrTiO_3$	0.2gr 5%,10gr.	50	-0.24	-0.26	-0.30	0.43
		70	-0.21	-0.24	-0.26	0.43
$BaTiO_3$,	0.2gr.5%,10gr.	50	-0.21	-0.26	-0.29	0.23
		70	-0.20	-0.24	-0.27	0.15
ThO_2, 0.2gr.	5%,10gr.	50	-0.23	-0.28	-0.35	0.57
		70	-0.23	-0.25	-0.29	0.37
$Mg_2(P_2O_7)$,0.2g	5%,10gr.	50	-0.21	-0.29	-0.35	0.37
		70	-0.21	-0.25	-0.30	0.32
Fuel cell grade asbestos						
10 mil		50	-0.33	-0.30	-0.31	0.16
(control)		70	-0.28	-0.28	-0.36	0.14

*Cast on Nylon Screen

IV. PHASE III. FULL CELL TESTING

A. TESTING APPARATUS AND PROCEDURE

Figure 5 is a schematic diagram of the test setup; Figure 6 illustrates the cell assembly used for testing.

This testing apparatus was originally designed for specific engineering studies of fuel cell operation in the project, "Study of Fuel Cells Using Storable Rocket Propellants", under NASA contract NAS3-4175. Consequently, the apparatus is essentially unsuitable for obtaining fundamental or highly quantitative data such as that obtained in half cell experiments. However, information obtained by this testing is valid as far as engineering problems connected with scaling up the size of cells and by operating large cells for prolonged periods.

In the setup shown in Figure 5, 5M KOH electrolyte containing initially 2M N_2H_4 was circulated over the anode surface by natural convection forced by evolving gas. Air flow rate was maintained at 4 times stoichiometric according to the reaction $O_2 + 2H_2O \rightarrow 4OH^- - 4e^-$ to obtain steady potentials of operating cells. The potentials of the electrodes were measured against a saturated calomel electrode immersed in the electrolyte reservoir. Consequently, these readings included IR drop through the cell. These electrode potentials and full cell potentials were used mainly as criteria to determine the useful life of the cells. At the time of failure (at an end of an active cell life), an analysis was made to determine the causes of failure.

A small amount of N_2H_4 corresponding to the amount that was consumed by the cell reaction was added continuously to the electrolyte reservoir by an automatic feeding device, and all of the electrolyte was renewed at least once a week in order to avoid the possible effect of adding impurities such as $CO_3^=$ and Fe ion to the system. The temperature of the system was controlled in the electrolyte reservoir at $70 \pm 2°C$. Consequently, the temperature of the cell was somewhat lower (in general approximately 65°C).

The rate of gas evolution was measured at least once a week by the water displacement technique.

B. SULFUR-POISONED ELECTRODE

In addition to the electrode that has been continuously tested since the last quarter, some new sulfur-poisoned electrodes have been tested.

Results are summarized in Table 6.
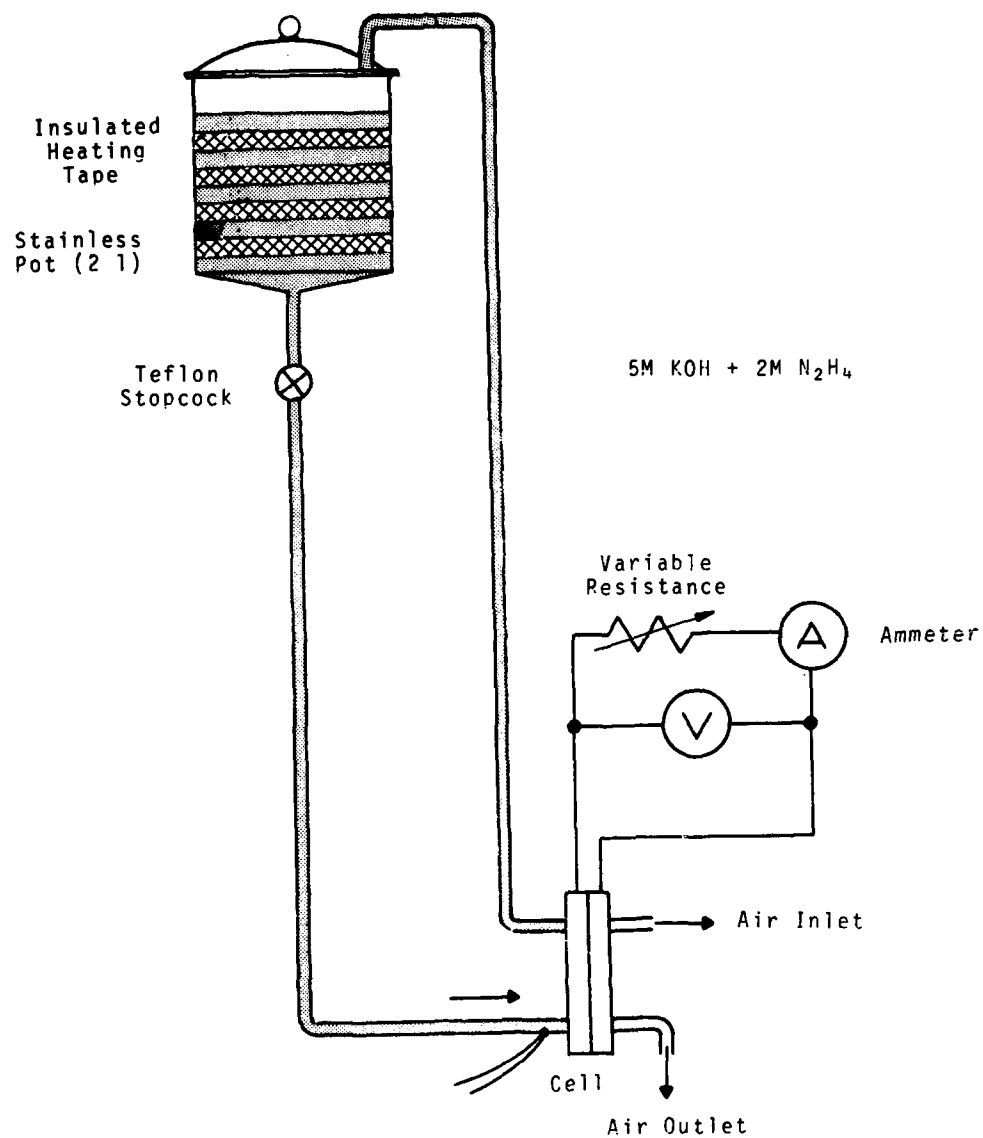
Figure 5.   Schematic Diagram of 3 x 3 in. Full Cell Test Setup.
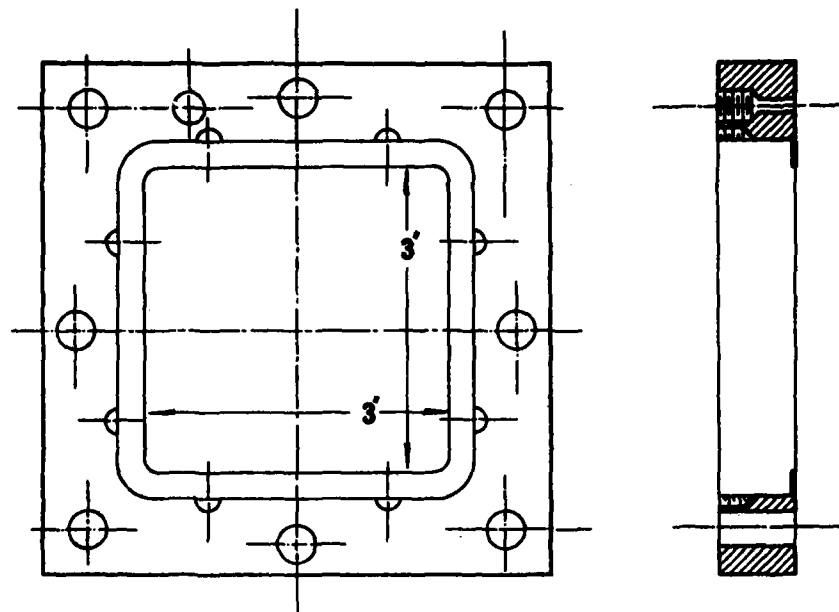
a. Cell Frame
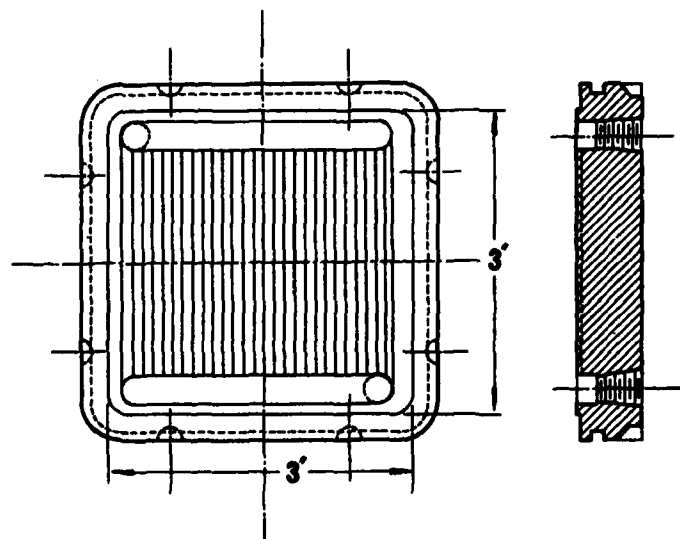
b. Cell Insert

Figure 6. 3 x 3 in. Full Cell Test Fixture.

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TABLE 6

3 x 3 INCH FULL CELL TESTS ON SULFUR POISONED ELECTRODE

No.	Description of Anode	Potential vs SCE at 100mA/cm²		Hours of Operation	Excess Gasing Rate %	Related Cathode Performance
		At Beginning	At the End			
1.	MRC Anode with 10^{-4}M Na₂S treatment for 24 hrs	-1.15	-1.18	4056	0	Excellent-2 Cathodes (2566 hrs & 1390 hrs)
2.	Ni plaque +6mg/inch² Pd with 10^{-4}M Na₂S treatment for 24 hrs	-1.17	-1.17	3768	12.0	Better than average- 4 Cathodes (1,100; 560; 920 & 1170 hours)
3.	MRC Anode with 10^{-4}M Na₂S treatment for 24 hrs	-1.14	-1.18	878	25.0	Average (878 hrs)
4.	MRC Anode with 10^{-3}M Na₂Se treatment for 24 hrs	-1.11	-1.12	768	0.0	Average (768 hrs)
5.	MRC Anode with dark Pd Plating, with 10^{-4}M Na₂S treatment for 24 hrs	-1.16	-1.17	1,488	0.0	Better than average- (1,488 hours)

As previously noted, the general performance of cathodes with these anodes were better than the average performance of MRC cathodes.

C. NEW TYPE ANODES

Full cell tests on new type electrodes were also started during the fourth quarter. Three electrodes of fibrous nickel membrane have been tested so far, but results were rather discouraging. These electrodes not only showed low potentials themselves but also seemed to shorten the useful life of cathodes.

V. WORK PLANNED FOR THE FIFTH QUARTER

Work planned for the fifth quarter includes the following:

(1) Determination of parameters affecting NH_3 formation (KOH concentration, N_2H_4 concentration, temperature and $CO_3^=$ contamination).

(2) Continuation of inexpensive (non-noble-metal) catalysts - testing on interstitial compounds.

(3) Continuation of study of separator materials.

(4) Continuation of study of NH_3 decomposition reactor - design of a prototype reactor and tests under other simulated conditions.

(5) 3 x 3 inch full cell testing on improved electrodes.

(6) Preliminary experiments on study of common electrolyte problems.

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13. ABSTRACT

In the fourth quarter, new materials for anode and separator were investigated, and experiments were carried out to optimize the treatment of anode with catalyst poisons ($S^=$), and the catalyst loading for NH_3 oxidation. Full cell testing (3 x 3 in.) again revealed the significant improvement in performance of both the hydrazine anode and also of the combined cathode imparted by $S^=$ poisoning. Very active non-noble-metal catalysts such as Ni-B, Co-B and Ni-P can be used if the electrode is properly poisoned. Generally, these catalysts give very active potentials but low fuel efficiencies by excess decomposition of hydrazine fuel.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fuel cells Hydrazine Electrocatalysts Electro-oxidation Fuel cell electrolytes Fuel cell reactions Hydrazine-air fuel cell						

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